Materials Science Forum Vols. 404-407 (2002) pp. 413-418

Ferroelastic Behavior of PZT-Based Ferroelectric Ceramics

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Keywords: Ferroelectric, ferroelastic, piezoelectric, PZT, neutron diffraction.

Abstract. As a first step towards developing accurate constitutive relations for ferroelectrics, neutron diffraction experiments were conducted on $Pb(Zr,Ti)O_3$ (PZT)-based polycrystalline ceramics. Elastic lattice strain and texture evolution were monitored *in situ* during uniaxial compression experiments. Single phase (tetragonal) PZTs as well as those at the morphotropic phase boundary (with tetragonal and rhombohedral phases present) were investigated.

Introduction

Ferroelectric ceramics are widely used in a diverse set of devices including sensors, actuators, transducers, and ultrasonic motors. In these applications, they exhibit a complicated behavior as they respond to both electrical and mechanical loading. During this process large internal stresses are generated which eventually lead to failure. Efforts to model and predict the behavior of ferroelectrics have often been hindered by the lack of suitable constitutive relations that accurately describe the electromechanical response of these materials. Recently, some self-consistent models have been developed to describe the behavior of polycrystalline ferroelectrics [1]. These models are essentially an adaptation of the self-consistent crystal plasticity scheme developed by Hill and Hutchinson and are able to capture some important features of ferroelectric behavior such as electro-mechanical hysteresis. However, in their current form, the models require further improvement. The formulation of robust models for ferroelectric materials requires knowledge of their crystallographic behavior under applied mechanical and electrical loading. Neutron diffraction is an ideal probe of bulk crystallographic structure and thus offers the possibility of observing ferroelectric constitutive behavior *in situ*. For the first time, this method was used to study internal strain and texture evolution in ferroelectric materials under mechanical loading. This article presents preliminary results from this investigation.

Experimental

Single phase tetragonal $Pb(Zr,Ti)O_3$ (PZT) specimens as well as samples at the morphotropic phase boundary (with both tetragonal and rhombohedral phases present) were obtained in solid form from American Piezo Ceramics, Inc. (Mackeyville, PA 17750, USA) and Robert Bosch GmbH (Stuttgart, Germany), respectively. Single phase samples were cylindrical in shape and measured approximately 6.35 mm in diameter by 16 mm in length. Morphotropic samples were rectangular, measuring 8 x 8 x 19 mm. Single phase samples were pre-poled by the manufacturer, while morphotropic samples were initially unpoled. The microstructure of specimens was investigated with scanning electron microscopy (SEM) and their chemical composition was determined with an electron probe analyzer (Jeol JXA-733 SEM equipped with wavelength-dispersive spectrometers).

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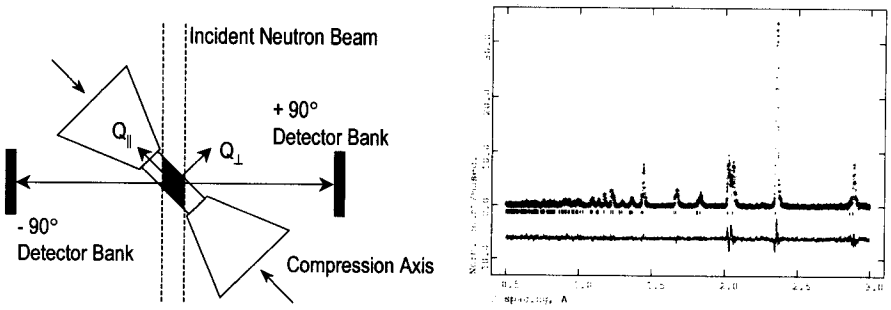
Published in 'Residual Stresses', Year: 2002, pp: 413-418
Periodical: Materials Science Forum Vols. 404-407
Published on http://www.scientific.net, eMail: office@scientific.net

The Zr/Ti ration was measured to be approximately 49/51 in the single phase samples and 52/48 in the morphotropic samples (these numbers include small amounts of dopants). These investigations also revealed the presence of small, heavy element inclusions within the PZT matrix in both samples. Measuring in size approximately 3 – 10 μm in diameter, the proportion of these inclusions with respect to the matrix composition has not been formally studied, nor is an analysis noted in the literature. It is probable that these inclusions may be small pockets of the initial reactants as PZTs are often prepared using ceramic methods with excess ingredients. Further analysis of the composition and structure of these inclusions is needed, as well as a formal assessment of their possible effects on measured data.

Neutron diffraction experiments were undertaken at the Rutherford Appleton Laboratory's ISIS Facility (UK) in the ENGIN diffractometer. *In-situ* time-of-flight neutron diffraction patterns of PZT samples were obtained at various compressive loads [2]. Observation of both the axial and transverse strains was possible due to the sample orientation and the detector geometry, see Fig. 1(a). Strain gauges attached to the samples measured macroscopic axial strain in the case of the single phase samples, and both the axial and transverse strain in the morphotropic samples. Data acquisition times were approximately 1.5 hrs per load level, during which time the samples were held at a constant load.



(a) (b)

Figure 1. (a) Schematic setup of neutron powder diffraction experiments. The scattering vectors for each detector indicate the direction of lattice strain measurements relative to the loading axis. (b) Typical diffraction pattern from a single phase PZT

Results and Discussion

Single Phase PZT. Strain gauge data for a tetragonal single phase sample in compression is shown in Fig. 2. The initial elastic region is very small, below –25 MPa. Notice the large changes in strain during the load changes between −25 and −100 MPa. This range corresponds to that of 90° and 180° domain switching in the sample. Upon reaching −150 MPa, the switching process has saturated and the sample's polarization vector has vanished due to the cylindrical symmetry of the sample (the individual dipoles are aligned with the normal of the cylindrical surface). At stresses greater than −150 MPa, the material again exhibits simple elastic behavior. Without a force impetus to return to their initial configuration, most of the domains remain in their switched position, an effect of the well-known electro-mechanical hysteresis exhibited by these materials. This results in large residual strains in the longitudinal direction upon unloading, as seen in Fig 2.

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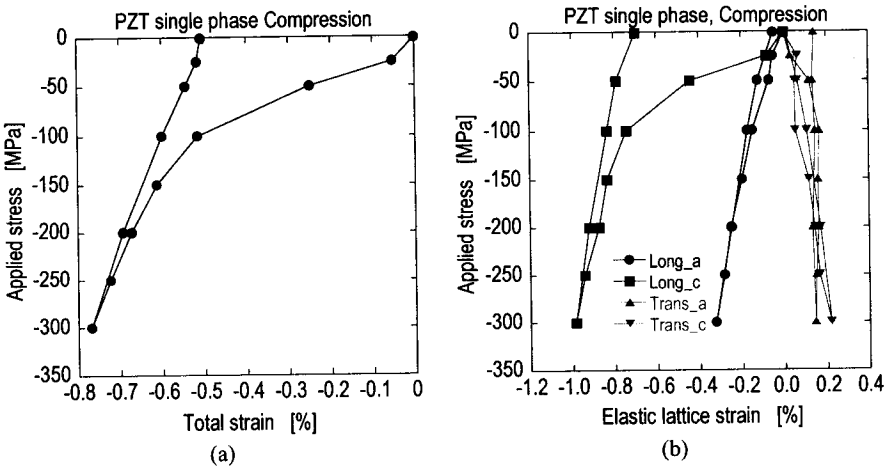

Figure 2. (a) Measured macroscopic stress-strain curve. (b) Measured diffraction stress-strain curve, for the single phase PZT. "Long" refers to parallel to the loading axis and "Trans" refers to perpendicular to the loading axis. "a" and "c" refer to the *a* and *c* lattice parameters, respectively.

Neutron spectra were analyzed with the Rietveld method [3] using the GSAS software package [4], see Fig. 1(b). Analysis of the single phase neutron spectra began using crystallographic data garnered from previous studies in the literature [5]. The crystal structure was described as the non-centrosymmetric space group *P4mm* [5, 6]. Atomic occupancies were inputted from the electron microprobe analysis and were not refined. Isotropic thermal parameters were constrained to be the same for crystallographically identical sites (dopant atoms had the same values as the atoms they replaced) in order to reduce the number of free parameters. Texture was accommodated by the spherical harmonic model [4] using 11 coefficients. The background was emulated using a Fourier cosine series with six terms. Peak profiles were defined by a back-to-back exponential pseudo-Voigt function (TOF function #3 in [7]), and the absorption correction was taken to be linear. Lattice parameters, isotropic thermal parameters, absorption and background coefficients, histogram scaling parameters, texture variables, and peak profile parameters were included in the refinement one at a time, and were refined simultaneously for the final fit.

The final discrepancies between the calculated neutron spectrum and the measured diffraction data as quantified by the weighted residual parameter (R_{wp}) [8] hovered around 18%. While these residuals are generally considered high by Rietveld standards, they are not without precedent. PZTs and similarly structured piezoelectrics are notoriously difficult to perform accurate Rietveld refinements on: negative thermal parameters and anomalous atomic positions are the most commonly encountered problems [5, 6, 9] Possible sources of error are the presence of a small amount of a rhombohedral phase [10], or the existence of inclusions of initial reactants (as noted in the current specimens). Especially problematic areas were the (200)-(002) doublet area around 2.1 Å and the prominent (111) peak at 2.35 Å, (see Fig 1(b)).

All attempts to improve the correlation between the measured and calculated data from within the framework of a tetragonal system failed. Negative thermal parameters, unreasonable absorption coefficients, and catastrophically displaced atomic positions were all encountered, while the general fit quality was always unstable with only slightly improved R_{wp} values. Because the two most mismatched areas of the diffraction pattern coincided with the areas where a secondary rhombohedral phase would contribute most significantly to the total intensity [5, 10], it was

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believed that including a slight amount of this secondary phase would both improve and stabilize the fits. This, however, was not the case. Adding a rhombohedral phase induced runaway correlations between several sets of physically related variables, which produced erroneous phase fractions. Any attempts to control the phase fractions led to completely unrealistic peak widths in the minority rhombohedral phase that allowed the various lattice parameters in both phases to attain unreasonable and unrepeatable values. In short, after experimenting with several different models and fitting procedures, a single phase tetragonal model was used for its simplicity and stability.

The texture observed in the sample changed significantly over the course of loading and unloading due to domain switching, as evidenced by large changes in the relative intensity of the (200) and (002) peaks (measured in the direction parallel to the loading axis). Fig 1(b) shows that these two intensities were approximately equal in the original poled, unstressed state. At higher loads, the intensity for the (002) peak was nearly zero. This is consistent with the switching of domains that initially were oriented with the *c* axis parallel to the loading axis into a 90° orientation (corresponding to the *c* axis being aligned perpendicular to the loading axis). The result is that the strain measured by diffraction for the *c* axis parallel to the loading axis shows a large compressive change during loading. Since the switching process is mostly not reversed during unloading, the strain cannot be relaxed, thus leaving a large negative residual strain of about 0.7%. The *a* axis parallel to the loading direction does not show the same large residual strains nor large strains under load, but does show a residual strain on the order of 500 $\mu\varepsilon$ ($\mu\varepsilon = 10^{-6}$). The transverse strains are small compared to the longitudinal (although still large compared to internal strains in more conventional materials). In this sample direction it is the *a* axis which shows a residual strain (about 0.15%) whereas the *c* axis does not.

Two Phase PZT. For the two phase PZT (at the morphotropic phase boundary), we could refine both the tetragonal phase and the rhombohedral phase, but due to the strong texture development during the loading test, the phase fractions were not reliable. This is because of the lack of detailed angular information of the texture in the sample. To accurately model the texture in the spherical harmonic model, multiple diffraction patterns recorded at several different angular orientations are needed. In the case of the single phase sample, this requirement can be relaxed, as there is only one phase contributing to the diffracted intensity. In the morphotropic samples, however, the convolutions of the intensities of two phases cannot be simply modeled from data collected at only two detector banks. Thus correlations between the texture variables and the phase fractions could not be prevented. Despite this caveat, strain information could still be retrieved from the diffraction data. Refinements proceeded much the same as in the case of the single phase sample. Lattice parameters, isotropic thermal parameters, absorption and background coefficients, histogram scaling parameters, texture variables, and peak profile parameters were eventually refined simultaneously for both phases. The final R_{wp} values for the morphotropic sample were slightly higher than those for the single phase material.

The diffraction data for the *c* axis of the tetragonal phase of the morphotropic sample show the same trend parallel to the loading axis as the single phase sample with a large residual strain (Fig. 3). However, the *a* axis of the tetragonal phase in the morphotropic sample shows an unexpected tensile residual strain of 280 $\mu\varepsilon$. Both *a* and *c* axes of the rhombohedral phase show similar trends as the *c* axis for the tetragonal phase with large compressive residual strains. Perpendicular to the loading axis there is relatively small residual and loading strains for the tetragonal *a* and *c* axes, and somewhat higher for the rhombohedral *a* and *c* axes. Further study of this material is currently underway.

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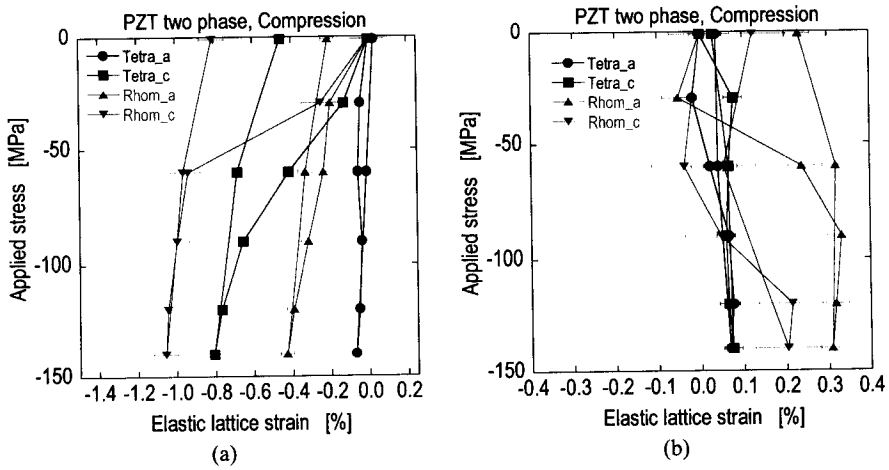

Figure 3: Measured diffraction stress strain curves: (a) parallel to, and (b) transverse to the loading axis, for the two phase PZT. "Tetra" refers to the tetragonal phase and "Rhom" refers to the rhombohedral phase. "a" and "c" refer to the *a* and *c* lattice parameters, respectively.

Conclusions

In-situ neutron diffraction can directly observe the ferroelastic constituative behavior of ferroelectric materials and provides information vital to the fomulation of accurate self-consistent models of these materials. The strains calculated from the diffraction data showed the same trends for the single phase and two phase samples: large residual strains along the *c* axes and small residual strains along the *a* axes parallel to the loading direction. Simultaneously, the texture of the samples changed radically as the domains initially oriented with the *c* axis along the loading directions switched 90° to accommodate the applied stress.

Difficulties in the fitting procedures and the high R_{wp} values indicate that our single phase tetragonal model is not completely adequate. Higher resolution spectra are needed to produce more accurate crystallographic models. The (200)-(002) doublet and the (111) peak are especially important because of their intensity and breadth. Preliminary X-ray diffraction studies at the Advanced Photon Source (Argonne National Laboratory) have clearly shown three distinguishable peaks in the (200)-(002) region of the morphotropic samples (two from the tetragonal phase and one from the rhombohedral phase), indicating that dual phase refinements should be possible. Future X-ray diffraction experiments will probe the ferroelastic-ferroelectic coupling in these materials *in situ* under high resolution, supplementing the ferroelastic information reported here. The adaption of the current data to existing self-consistent models [1] is also underway and will be reported in a future publication.

Acknowledgments

This study is supported by the Multidisciplinary University Research Initiative at Caltech on Engineering Microstructural Complexity in Ferroelectric Devices (Army Research Office grant no. DAAD19-01-1-0517) and the National Science Foundation (CAREER grant no. DMR-9985264). The authors also acknowledge insightful discussions with Professor R. M. McMeeking from the University of California, Santa Barbara.

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Periodical: Materials Science Forum Vols. 404-407
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